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CORROSION STUDIES IN MOLTEN ALKALI CARBONATES

PART III, GOLD-PALLADIUM, NICKEL, AND STAINLESS STEEL-347

by

G.J. Janz and A. Conte

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, N.Y.

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CORROSION OF GOLD-PALLADIUM, NICKEL, AND STAINLESS STEEL (347) IN MOLTEN ALKALI CARBONATES

by

George J. Janz and A. Conte[+]

Rensselaer Polytechnic Institute, Department of Chemistry, Troy, N.Y.

Results are reported on the ability of gold-palladium, nickel, and columbium-stabilized stainless steel to withstand chemical attack in molten alkali carbonates for prolonged periods at high temperatures (600° - 700°C). The nature of the products formed, and the extent of corrosion were investigated as an extension of the studies on the noble metals, silver, and refractories described in the preceding communication.[1]

EXPERIMENTAL AND RESULTS

The preparation of the ternary eutectic mixture of Li_2CO_3, Na_2CO_3 and K_2CO_3 and the apparatus for the weight-loss corrosion tests have been given in detail elsewhere[1]; it is sufficient to note that CO_2 gas atmosphere (1 atm press) was maintained above the melt for all the measurements. The metals, highest purity specimens commercially available, were used without further treatment.

To gain information on the nature of the products formed, a series of measurements were undertaken for prolonged periods at 700°C as described previously[1]. After the experiments, the specimens were boiled in water to remove carbonates and soluble corrosion products. The nature of the film on

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[+] Post-Doctoral Research Fellow: Present Address: Laboratorio di Chimica delle Radiazioni e Chimica Nucleare, Istituto di Chimica Generale, Citta Universitaria, Roma, Italia.

the surface of the specimens was examined by X-ray diffraction methods (Cu K_α; 35 kV; 10 ma; 6-12 hrs). The results for the nickel and 347 stainless steel tests are in Table 1 together with the literature values[2] for NiO and $LiFeO_2$. On the Au-20% Pd alloy surface, after such tests, a faintly colored film was visible to the eye; X-ray results only confirmed the presence of the unchanged alloy surface. The thickness of the film was apparently insufficient for the conventional X-ray diffraction methods and this work was not pursued further.

A series of weight-loss measurements for each specimen in the presence of added oxides in the carbonate melts (by virtue of the sintered Al_2O_3 crucible technique[1]) and in the pure carbonate melts were also undertaken to gain some quantitative measure of the ability of these metals to withstand corrosion. The results are in Table 2.

DISCUSSION

The X-ray diffraction data (Table 1) leave little doubt that the products for the chemical attack by molten carbonates at 700°C on nickel and 347 stainless steel are, respectively, NiO and $LiFeO_2$. The nature of the product of the small but finite attack of the Au-Pd (20%) alloy can be inferred from the known formation[3] of sodium palladiate when palladium is exposed to molten Na_2CO_3; the film detected by visual inspection is likely an oxide (possibly a palladiate), but exact confirmation must await additional analytical studies.

The nickel attack was further investigated by using a pure nickel crucible to contain the molten carbonates at 600°C and at 710°C for 24 hour periods, respectively. At the lower temperature the crucible walls were

uniformly covered with the oxide coating; at the higher temperature the oxide coating was severe and the crucible walls were embrittled. It is known[4] that intercrystalline precipitation of graphite and NiO occurs when nickel is exposed at elevated temperatures to carburizing atmospheres. This factor and the possible formation for NiO through the decomposition at 600-700°C of the thermodynamically unstable $NiCO_3$ being formed as a "soluble" corrosion product, are undoubtedly contributing factors to the nickel corrosion processes under the environmental conditions of these experiments.

The weight-loss experiments (Table 2) show that the changes in the presence of added oxide ions (i.e. Al_2O_3) are as would be predicted in the Mass Law shifts for the overall equilibria of the type:

$$[2M^{+} + CO_3^{=}]_l \rightleftharpoons 2M + CO_2 + \tfrac{1}{2}O_2$$

and

$$[2M^{+} + O^{=}]_l \rightleftharpoons 2M + \tfrac{1}{2}O_2 \qquad (1)$$

The oxidant initiating the metal attack is undoubtedly present as an impurity in trace amounts; rigorous exclusion of air (oxygen) in such melts is difficult.

Comparison of the results for the niobium-stainless steel (347) with Au-Pd (20%) in Table 2, and the noble metals in the preceding communication[1] reveals that this metal is quite highly resistant to attack; the oxide film ($LiFeO_2$) suggests the possibility of passivity. It is known that passivity can be conferred by use of a galvanic couple of the active-passive specimen and a more noble metal[5]. The result of such an exploratory experiment is given in Table 2. A small but significant measure of protection can be inferred if the decreased weight change is truly significant. Electrochemical studies using a potentiostatic polarization technique are being initiated in This Laboratory to gain additional information on these processes.

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We thank Dr. Norbert D. Greene for helpful discussions, particularly relative to the exploratory galvanic couple experiment. This work was made possible, in large part, by financial support from the U.S. Department of the Navy, Office of Naval Research, Chemistry Division, Washington, D.C.

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TABLE 1

DEBYE-SCHERRER X-RAY RESULTS FOR CORROSION PRODUCTS

Nickel in Molten Carbonates

d(Å) obs'd	2.09	2.41	1.48
intensity	v.s.	s.	m.
d(Å) literature (NiO)	2.09	2.41	1.48

Type 347 Stainless Steel in Molten Carbonates

d(Å) obs'd	2.06	1.47	2.39
intensity	s.	m.	w.
d(Å) literature* ($LiFeO_2$)	2.07	1.47	2.39

*literature values taken for A.S.T.M. X-Ray Diffraction Reference Index (1962)

Table 2

STATIC CORROSION EXPERIMENTS: Au-20% Pd ALLOY, NICKEL AND TYPE 347 STAINLESS STEEL IN THE MOLTEN Li, Na, AND K CARBONATE EUTECTIC MIXTURE UNDER CO_2 ATMOSPHERES

Temperature (°C)	Crucible Type	Time (Hrs)	Sample Area (cm^2)	Sample Change mg hr cm^{-2}
	Au-20% Pd Alloy			
740°	sintered Al_2O_3	96	1.90	+0.001
740°	Au-20% Pd	96	2.63	+0.010
	Nickel			
670°	sintered Al_2O_3	63	2.16	-0.010
670°	Au	63	2.60	-0.017
	Type 347 Stainless Steel			
730°	sintered Al_2O_3	94	-5.0	-0.003
730°	Au-20% Pd	95	5.5	+0.023
730°	Au-20% Pd	93	8.2‡	+0.016

‡ The stainless-steel sample was galvanically coupled with platinum, both totally immersed in the melt.

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